10/533295
JC17 Rec'd PCT/PTO 29 APR 2005

Sandvik AB

Use of a corrosion-resistant, maraging steel

Technical field

The invention relates to a novel use for precipitation-hardenable, martensitic, stainless steels for the manufacture of rotary tools for applications with high requirements as regards a combination of high hardness and ductility as well as corrosion resistance, such as drilling, milling, grinding and cutting tools.

Background and technical problem posed

Precipitation-hardenable, martensitic, stainless steels are known from WO 93/07303. In this a composition of a stainless steel is described which has a very high strength with simultaneously good ductility. This steel is described as being particularly suitable for the manufacture of injection cannulae, dental instruments and medical instruments on the basis of wire and strip material produced from the named types of steel. Because of the high hardness of the steel, further working had to be restricted to a minimum.

In WO 01/14601 A1 a process is described for the manufacture of parts with complicated geometry by a series of process steps, including precipitation hardening, annealing, quenching and hardening, the result of which is a homogeneous hardness of at least 450 HV. It is mentioned by way of example that a precipitation-hardenable, martensitic, stainless steel can be used for the manufacture of medical instruments according to the process specified therein. The problem of workability was solved in this case with the help of the special manufacturing process, but this cannot be applied to tools, especially rotary tools with complicated geometry.

A range of boundary conditions should be satisfied for the use of a steel for the manufacture of machine-operated rotary tools, in particular rotary tools for medical, especially dental and surgical applications.

Drills, milling, grinding and cutting tools have very small diameters, according to their intended use, which can be less than 1 mm. However their length is great in relation to the diameter in order to make possible a specific working depth and is further increased by the section which is provided for the housing of the tool in the tool holder or chuck. Because of this extreme length/diameter ratio and the resulting unfavourable moment distribution, such tools are very sensitive to the bending loads applied in practical use. A slight bending, barely visible to the naked eye, of the drill can result in its generally running untrue and being unbalanced when next prepared by the operator or next used. Because of the frequently very high rotation speeds this results, in practice, in the drill bits breaking

off during operation. This means not only that the drills have a short life and must frequently be replaced for reasons of safety, but also that there is a substantial risk of injury for operator, patient and bystanders who may be hit by flying parts of tools, as well as a substantial cost factor.

According to the Medical Products Law, tools with small dimensions in particular are designated disposable products by manufacturers, which represents an additional cost for the user. After the tools have been used once their use on a second occasion is no longer allowed, and the user must use a new tool, which leads to unreasonably high costs.

There is therefore an urgent need for machine-operated rotary tools for multiple use, in particular dental and surgical drilling, milling, grinding and cutting tools with and without a defined cutting edge which have a very high hardness, are corrosion-resistant and at the same time are also fracture-proof vis-à-vis known tools or instruments. In addition to hardness and fracture resistance the simultaneous corrosion resistance is of crucial importance. Dental and surgical instruments are sterilized after every use and exposed to strongly corrosive conditions (temperature, moisture, organic and other solvents etc.). In addition there are the corrosive media during use, such as e.g. blood and other bodily fluids. If such dental and surgical instruments are damaged or attacked by corrosion, there is the danger of patients being contaminated by the corrosion residues and exposed to dangerous post-operative complications.

There is therefore an urgent need for stable, corrosion-resistant and biocompatible machine-operated rotary tools, such as drilling, milling, grinding and cutting tools, which simultaneously offer high strength values, combined with good ductility properties.

At present a range of well-known and well-tested alloy types is used for shaping and manufacturing such tools and instruments. Some of these alloys are martensitic rustless steels, austenitic rustless steels and precipitation-hardenable rustless steels. Each of these known alloys has a series of good material properties, such as corrosion resistance, strength, mouldability and/or ductility, but each alloy also has disadvantages and cannot satisfy specific product requirements. Complex problems and disadvantages of rotary tools currently available on the market are known from practice. The following table shows the compositions of some frequently used steels.

Alloy	C	Si	Mn	S	Cr	In	Mo	Cu	Ti	N	P
AISI 420	0.360	0.15	0.30	<0.020	13.5	<0.3					
AISI 420 F	0.220	0.58	1.58	0.175	13.0	0.80	1.2				
AISI 304	0.060	0.66	1.22	0.002	18.6	8.60	0.2				
ISO 5832-1-D	<0.03	<1.0	<2.0	<0.01	17.5	14.0	2.8	<0.5		<0.1	<0.025
ISO 5832-9	0.080	<0.75	3.60	<0.01	20.5	10.0	2.5	<0.25		0.4	<0.025
Carpenter 455	0.006	0.07	0.03	0.004	11.40	8.30	<0.1	2.2	1.2		

C455 (V)	0.004	0.04	0.15	0.002	11.80	9.10	<0.1	2.0	1.6		
1.4108	0.310	0.68	0.41	0.002	15.54	0.16	0.97			0.41	0.017
1.4112	0.85-0.95	<1.0	<1.0	0.030	17.0-19.0		0.9-1.3				0.040

Table 1: Compositions of various known steels in wt.-%; remainder iron

Martensitic, rustless steels, e.g. the AISI 420 grades, can offer a high strength but not in combination with ductility. Austenitic rustless steels, e.g. the AISI 300 range, can offer good corrosion resistance in combination with high strength and ductility acceptable for some applications, but a marked cold reduction is required to achieve the high strength, and this means that the semi-finished product must also have a very high strength, which in turn leads to poor mouldability. For the group of the precipitation-hardenable, rustless steels there are numerous different grades with different properties. However they have some features in common, for example most of them are vacuum-melted in a one-way or more usually in a two-way process, the second step being a melt-on under vacuum. Furthermore, a large quantity, i.e. >1.5 wt.-% of precipitation-forming elements, such as aluminium, niobium, tantalum and titanium, is required, often also as a combination of these elements. A large quantity is favourable for strength, but reduces ductility and mouldability. Such a grade is found e.g. in US patent specification 3,408,871. This grade offers an acceptable ductility in the finished product in combination with a strength of only approximately 2,000 N/mm^2. It can also have disadvantages during manufacture of semi-finished products, e.g. this steel is susceptible to cracking in the annealed state.

Description of the invention

The object of the present invention is to overcome the aforementioned problems and disadvantages of the state of the art.

This object is achieved according to the invention through the use of a precipitation-hardenable, martensitic, rustless chrome nickel steel with the following composition (in wt.-%):

Chromium	10 to 14
Nickel	7 to 11
Molybdenum	0.5 to 6
Copper	0.5 to 4
Aluminium	0.05 to 0.55
Titanium	0.4 to 1.4
Carbon + nitrogen	up to 0.3
Sulphur	less than 0.05
Phosphorus	less than 0.05
Manganese	up to 0.5

Silicon	up to 0.5
Tantalum, niobium, vanadium and tungsten	each up to 0.2
Cobalt	where appropriate up to 9.0
Boron	where appropriate 0.0001 to 0.1

the remainder comprising iron and customary impurities,

for the manufacture of machine-operated rotary tools.

This object according to the invention is further achieved by the provision of machine-operated rotary tools which are made from precipitation-hardenable, martensitic, rustless chrome nickel steel with the aforementioned composition.

Rotary tools according to the invention are preferably drilling, milling, grinding and cutting tools with or without geometrically defined cutting edges, particularly preferably machine-operated rotary cutting machine tools according to DIN 8580. As a rule, such a tool comprises a shaft, a machining tool head and a mounting part. The tool is moved axially and/or transversely. A surprising effect, covered by the invention, is that precipitation-hardenable, martensitic, stainless steel used in accordance with the invention is advantageous in applications in which the combination of high fracture and bending resistance with hardening and corrosion properties plays a crucial role.

In a particularly preferred version of the invention the rotary tools are medical tools and instruments, in particular for dental and surgical application.

A further surprising effect, covered by the invention, relates to the advantageous combination of good biological compatibility of the precipitation-hardenable, martensitic, rustless steel used according to the invention with good corrosion properties, high ductility and outstandingly high strength of approximately 2,500 to 3,000 N/mm^2. This combination permits the advantageous use of this steel in medical applications in which the material remains in the body of the patient for a shorter or longer period of time.

A steel composition particularly suitable according to the invention contains for example 12.0 wt.-% chromium, 9.1 wt.-% nickel, 4.0 wt.-% molybdenum, 2.0 wt.-% copper, 0.9 wt.-% titanium, 0.35 wt.-% aluminium, <0.012 wt.-% carbon and <0.012 wt.-% nitrogen.

Description of the properties according to the invention

Tensile strength, elongation at fracture and hardness were tested on well-hardened solid-material workpieces of identical geometry from the steel used according to the invention and two other steels currently used for rotary tools.

The tested steel according to the invention is a composition according to the material 766685 given in table 2. Other embodiments can be seen in table 2.

Material	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Cu	Al
766685	0.008	0.12	0.18	0.009	0.001	12.19	9.16	3.99	1.08	1.99	0.33
766757	0.01	0.13	0.27	0.011	0.001	11.85	9.0	3.95	0.97	1.96	0.33
451234	0.004	0.22	0.25	0.015	0.001	11.85	9.14	3.99	0.86	1.95	0.36
769228	0.008	0.11	0.21	0.006	0.001	12.05	9.15	3.96	0.90	1.99	0.34
768276	0.009	0.09	0.19	0.01	0.002	12.15	9.02	3.99	0.9	1.99	0.30
769014	0.008	0.08	0.25	0.01	0.001	11.99	9.12	4.07	0.82	1.99	0.37

Table 2: Examples of steel compositions according to the invention

The grades 1.4112 and 1.4108, whose compositions are given in table 1, were used as comparison steels. The samples investigated were solid-material rods with a circular cross-section and a diameter of 4.5 mm. All the samples tested were precipitation-hardened. The hardening of the steel according to the invention took place at 475°C for 4 hours. The hardening of the grades 1.4112 and 1.4108 took place according to the hardening processes prescribed for these steels, at 1000°C for 40-60 minutes in vacuum. Both grades were then cooled to minus 50°C in nitrogen. The material 1.4108 was additionally tempered at 160°C for 2 hours. The described processes for manufacture and working of the reference materials give the highest possible values for hardness and ductility.

The hardening of the respective materials was carried out in such a way that a comparable material hardness was achieved for all the tested materials. Four samples of each material were tested. The results of the tensile test carried out according to DIN EN 10002-1 are summarized in the following table 3.

Material	**Tensile Strength [Mpa]**	**Elongation at break [%]**	**Rockwell C hardness**
766685	1935	9.1	52/53
766685	1938	9.1	52/53
766685	1941	9.1	52/53
766685	1946	9.1	52/53
1.4112	1989	<2	54/55
1.4112	1981	<2	54/55
1.4112	1987	<2	54/55
1.4112	2000	<2	54/55
1.4108	1323	<2	54/55
1.4108	1263	<2	54/55
1.4108	1153	<2	54/55
1.4108	1312	<2	54/55

Table 3: Test results, tensile test according to DIN EN 10002-1

An examination of the fracture points of the tested materials showed clearly that the steel according to the invention had an extremely tough fracture behaviour. The fracture faces had the form of a so-called hopper fracture. In contrast, the materials 1.4112 and 1.4108 showed so-called cleavage fractures with a near 100% brittle fracture content. The good breaking elongation behaviour of the samples made from the steel according to the invention is associated with a high flexibility, without the material breaking. The samples can be bent repeatedly without breaking. In contrast, the samples made from materials 1.4112 and 1.4108 broke the first time they were bent. The appended figure 2 shows at (A) the fracture surface of the comparison material 1.4108 and at (B) the material according to the invention bent under identical test conditions.

It was surprisingly shown that the utilization of the type of steel used according to the invention for the manufacture of machine-operated rotary tools, such as drilling, milling, grinding and cutting tools with and without a defined cutting edge, offers special advantages, in particular in dental and surgical applications, due to the outstanding ultimate breaking elongation behaviour of the steel grade compared with steels used hitherto. In the steels used hitherto, hardness and corrosion resistance in particular, as well as biocompatibility depending on the application, were to the fore. In respect of the tensile strength, a compromise has been accepted in the case of steels known hitherto. Through the use according to the invention of the present steel for the manufacture of machine-operated rotary tools, such as drilling, milling, grinding and cutting tools with and without a defined cutting edge, the disadvantages resulting from the fracture behaviour of the products obtainable on the market hitherto have now also been overcome. The tools produced according to the invention combine hardness, maximum corrosion resistance, good biocompatibility and outstanding breaking strength in the products manufactured. The products also remain fracture-resistant when bent and can be bent repeatedly, such as for example in plastic surgery, without sacrificing their outstanding material properties. In addition, the steel grades used according to the invention have good workability and good milling properties when hardened, which proves advantageous in the manufacture of the products. A further advantage of the use of the steel used according to the invention for the manufacture of rotary tools is the relatively low hardening temperature in the range 425 to 525°C, which results in substantial energy cost savings during manufacture.

If tools are approved for repeated use they must fulfil particularly high requirements in respect of the corrosion resistance of the steel during sterilization. Tools according to the invention were tested in accordance with DIN 1662 for their corrosion resistance. The test conditions defined in DIN 1662 were then transferred to the disinfection solutions listed in table 4 and tools then optically tested for traces of corrosion. Table 4 also shows the optical assessment appraisals. The tests were carried

out on tools with different surface finishes, i.e. ground, milled, electropolished and glass bead- or sand-blasted. As specific regulations apply to the identification of tools in the medical field, to prevent errors during use, particular attention has been paid to laser identification of same. Both the action of heat and also the areas which were more strongly mechanically worked, such as e.g. the cut faces of the rotary tools in question, are exposed to particular stress during use in corrosive media and during sterilization. Previous experience with these areas and the above-mentioned alloys have shown that faults and corrosion starting points induced there form. The optical assessment carried out of the tools according to the invention after the above-described corrosion test gave no indications whatsoever of corrosion or loss of material.

Disinfectant solution/Trade name	**Material(s)**	**Optical appraisal**
Sekusept Plus	Antimicrobial active ingredients, surfactants, corrosion inhibitors, phosphates, 10% sodium perborate, 10% tetracetylglycoluril	No traces of corrosion
Sekumatic FNP	Non-ionic surfactants, phosphoric acid (above 25%), corrosion inhibitors	No traces of corrosion
Sekumatic PRE	Below 5% non-ionic surfactants, above 30% phosphates, enzymes	No traces of corrosion
Ringer solution	Sodium chloride, potassium chloride, calcium chloride	No traces of corrosion
NaCl		No traces of corrosion
H_2O_2		No traces of corrosion
Neodisher FA	15-30% phosphates, 15-30% sodium and potassium silicates	No traces of corrosion
Hypochloride	NaClO	No traces of corrosion

Table 4: Corrosion resistance of tools manufactured according to the invention

As the corrosion results suggest that the material has a high corrosion resistance under both acid and alkaline application conditions, it is to be assumed that it is to be introduced with advantage for use as a rotary tool in ceramic materials, wood, plastic materials and steel and under the named environmental conditions.

Description of the figures

Figure 1 shows a possible version of the present invention in the form of a drill.

Figure 2 shows the surface of fracture (A) of the comparison material 1.4108 and the material (B) according to the invention bent under identical test conditions.

Figure 1 shows an embodiment of the present invention in the form of a drill for surgical use. The length/diameter ratio of the tool is in this case approx. 72:1. A length/diameter ratio of this order brings with it special requirements in respect of the flexural strength of the steel used, and these are met by the steel according to the invention, while avoiding the disadvantages named above.

Figure 2 shows at (A) the surface of fracture obtained in the bending test of the above-described material 1.4108 and at (B) the material according to the invention bent under identical test conditions.